TEMPERATURE DEPENDENCE IN RELATIVE POPULATIONS BETWEEN ISOMERS HAVING DISTINCT HYDROGEN BOND STRUCTURES OF PHENOL-METHANOL CLUSTER CATIONS

MASATAKA ORITO, MASAYOSHI OZEKI, HARUKI ISHIKAWA, *Department of Chemistry, School of Science, Kitasato University, Sagamihara, Japan.*

Gas-phase hydrogen-bonded clusters are treated as microscopic models of hydrogen bond networks. We have been investigating the temperature effect on microscopic hydrogen bond structures. In our previous study, we measured ultraviolet photodissociation (UVPD) spectra of hydrated phenol cations $[PhOH(H_2O)_5]^+$ trapped in our temperature-variable ion trap. We revealed temperature dependence of relative populations between two isomers having distinct hydrogen bond structures.[a] It is known that water and methanol molecules construct different hydrogen bond networks. Thus, we measured UVPD spectra of phenol-methanol cluster cations $[PhOH(MeOH)_n]^+$ ($n = 3, 4$) in the present study. As in the case of $[PhOH(H_2O)_5]^+$, isomers having ring type hydrogen bond structures are dominant in cold condition for both $n = 3$ and 4 cases. As the temperature elevates, populations of the chain type isomers become large in the case of the $n = 3$. Both bands for the ring and chain type isomers exhibit red shifts of the band positions and broadening of the band widths along the temperature elevation were observed. These changes were attributed mainly by hot bands of the intermolecular vibrational modes. In contrast, only the bands assigned as the ring isomers were observed with the temperature below 150 K. However, changes in the band profiles indicate structural changes within a ring type hydrogen bond motif.

[a]H. Ishikawa, I. Kurusu, R. Yagi, R. Kato, Y. Kasahara, *J. Phys. Chem. Lett.* **8**, 2641 (2017).